

APPLICATION  
FOR  
UNITED STATES LETTERS PATENT  
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PATENT APPLICATION  
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SPECIFICATION

TO ALL WHOM IT MAY CONCERN:

Be it known that David L. Carnahan of 671 Great Plain Avenue, Needham, MA 02492 has invented certain improvements in APPARATUS AND METHOD FOR NANOSCALE PATTERN GENERATION, of which the following description is a specification.

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APPARATUS AND METHOD FOR NANOSCALE PATTERN GENERATION

Reference To Pending Prior Patent Application

5 This patent application claims benefit of pending  
prior U.S. Provisional Patent Application Serial No.  
60/397,426, filed 07/19/02 by David L. Carnahan for  
APPARATUS AND METHOD FOR NANOSCALE PATTERN GENERATION,  
which patent application is hereby incorporated herein  
by reference.

10 Field Of The Invention

This invention relates to an apparatus and method  
for the patterning of nanoscale periodic structures  
using self-assembly of particles. The present  
15 invention is also directed to the use of these  
patterned arrays of regular particles, and the  
interstices between these particles, as a mask for the  
deposition of materials. Further, the present  
invention is directed to the formation of patterned  
20 arrays with periodicity that extends without defects  
over large areas. Still further, this invention is  
directed to the use of these arrays as masks for the

deposition of materials which are catalytic to the growth of carbon nanotubes by chemical vapor deposition methods.

5      Background Of The Invention

10      The trend of miniaturization of solid-state electronics is likely to continue. Therefore, the ability to create complex structures at the nanoscale level will rapidly become important to the electronics industry. Traditional lithographic methods are approaching theoretical limits, and will be unable to define truly nanoscale features. Therefore, an alternative technique to simultaneously produce many identical nanoscale structures would be advantageous in terms of efficiency and cost.

15      Micron-sized electronic components and circuits are commonplace, and rapidly being replaced by circuitry with several hundred nanometer features. In order to make further advancements in this area, mass production techniques are needed for the assembly of 20      10-100 nanometer features.

Optical lithographic processes are limited in final resolution by the wavelength of the light used to expose the photoresist. Alternative techniques, such as electron beam lithography, have been developed to overcome the limitations of optical light. However, electron beam lithography is difficult to employ in a massively parallel system and, therefore, is costly.

A number of inventive approaches have been proposed to enable the production of nanoscale features on various substrates. Nanosphere lithography (NSL) is one such approach which holds promise, if certain hurdles can be overcome. In NSL, an array of ordered, nanosized particles are deposited on a substrate, forming a mask that exposes the substrate at sites between the particles. A material can then be deposited through the mask, creating a periodic structure, as proposed by U.S. Patent No. 6,261,469, issued to Zakhidov et al.

To prepare an ordered array, particles are first dispersed in a liquid, then applied to a substrate, where the particles randomly assemble into a disordered mono or multilayer. As the liquid dries, capillary

forces act upon the particles to form close packed,  
hexagonal arrays. Kralchevsky & Nagayama (Langmuir,  
Vol. 10, No. 1, 1994) studied the theoretical aspects  
of this method of fabrication, understanding that when  
5 the liquid film thickness approaches that of the  
particle size, the particles are pulled together by  
surface tension. The formation of an ordered monolayer  
was first reported by Fischer and Zingsheim in 1981,  
where they prepared a suspension of 312 nm particles on  
10 a glass plate (U. Fischer, H. Zingsheim, J. Vac. Sci.  
Technol., Vol. 19, pp. 881, 1981). After evaporation  
of the solvent, small portions of the plate were  
covered by a monolayer of spherical particles. In some  
areas, the spheres were close packed. Subsequent  
15 vacuum deposition through the interstices between  
particles in the close packed section resulted in a  
hexagonal pattern of triangularly shaped deposits on  
the substrate. The interstitial size is approximately  
0.155 D, and the distance between adjacent deposits is  
20 approximately 0.8 D, where D is the diameter of the  
sphere.

Later, R. Micheletto (Langmuir, Vol. 11, pp. 3333, 1995) introduced a method to nucleate the hexagonal structure by tilting the substrate, which causes the organization to begin at the top of the substrate and continue downward as the drying and consolidation progresses. Dimitrov & Nagayama (Langmuir, Vol. 12, pp. 1303, 1996) modified this technique to slowly draw a plate from a bath of dispersed particles, resulting in the same effect.

However, the deficiency in all of the existing prior art is that these techniques do not form arrays with long range order. This is due to the existence of multiple nucleation sites, where the ordered arrays begin to form. When nucleation sites grow together, they must rotate or rearrange themselves if they are to mesh perfectly together, which does not happen in the techniques used in the prior art.

#### Summary Of The Invention

Accordingly, an object of the present invention is to provide apparatus for the synthesis of long range ordered arrays of particles on a substrate.

Another object of the present invention is to provide a method for synthesis of long range ordered arrays of particles on a substrate.

A further object of the invention is to provide a method for creating a deposition having a nanoscale pattern on a substrate.

With the above and other objects in view, as will hereinafter appear, there is provided apparatus for generating a mask having a nanoscale pattern, the apparatus comprising: a container having a top portion and a bottom portion, at least one sidewall between the top portion and the bottom portion, and an enclosed area formed by the top portion, the bottom portion and the at least one sidewall; a supporting liquid disposed within the container, the supporting liquid forming a top surface at a first given height between the bottom portion and top portion of the container, and the supporting liquid having a first given density; a substrate positionable within the container at a second given height from the bottom portion thereof, the substrate having a top surface disposed toward the top portion of the container; a suspension comprising a

suspension fluid having a plurality of particles  
suspended therein, the suspension being selectively  
deliverable to the enclosed area within the container,  
the suspension of the plurality of particles having a  
5 second given density, the second given density of the  
suspension configured to be less than the first given  
density of the supporting liquid; and adjustment means  
for adjusting at least one of the first given height of  
the top surface of the supporting liquid and the second  
10 given height of the top surface of the substrate  
relative to one another so as to transfer the plurality  
of particles within the suspension from a first  
position to a second position, wherein the first given  
height of the top surface of the supporting liquid is  
15 higher than the second given height of the top surface  
of the substrate at the first position and the first  
given height of the top surface of the fluid is lower  
than the second given height of the top surface of the  
substrate at the second position so as to deposit the  
20 plurality of particles onto the top surface of the  
substrate and generate a nanoscale pattern thereon.



In accordance with a further feature of the invention, there is provided a method for generating a mask having a nanoscale pattern, the method comprising: suspending a periodic arrangement of objects on a top surface of a supporting liquid at a first given height above a top surface of a substrate; and adjusting at least one from a group consisting of the top surface of the supporting liquid and the top surface of the substrate to position the top surface of the fluid below the top surface of the substrate so as to deposit the periodic arrangement of objects onto the top surface of the substrate from the suspension on the top surface of the supporting liquid; wherein the periodic arrangement of objects is maintained over a given area.

In accordance with a further feature of the invention, there is provided a method for creating a deposition having a nanoscale pattern on a substrate, the method comprising: suspending a periodic arrangement of objects on a top surface of a supporting liquid at a first given height above a top surface of a substrate; adjusting at least one from a group consisting of the top surface of the fluid and the top

surface of the substrate to position the top surface of  
the supporting liquid below the top surface of the  
substrate so as to deposit the periodic arrangement of  
objects onto the top surface of the substrate from the  
5 suspension of the top surface of the fluid, whereby to  
create a mask; and depositing a material through  
interstices contained in the mask so as to create a  
pattern on the substrate.

The above and other features of the invention,  
10 including various novel details of construction and  
combinations of parts and method steps, will now be  
more particularly described with reference to the  
accompanying drawings and pointed out in the claims.  
It will be understood that the particular devices and  
15 method steps embodying the invention are shown by way  
of illustration only and not as limitations of the  
invention. The principles and features of this  
invention may be employed in various and numerous  
embodiments without departing from the scope of the  
20 invention.

Brief Description Of The Drawings

These and other objects and features of the present invention will be more fully disclosed or rendered obvious by the following detailed description  
5 of the preferred embodiments of the invention, which are to be considered together with the accompanying drawings wherein like numbers refer to like parts, and further wherein:

10 Figs. 1A-1D are schematic views of apparatus for generating a mask having a nanoscale pattern;

Fig. 2 is schematic view of an embodiment of spheres arranged in nearly perfect crystal order;

Fig. 3 is a schematic view of electron beam evaporation of nickel onto the prepared substrate;

15 Fig. 4 is a schematic view of deposition of a material through the interstitial spaces of the mask which results in triangular shaped deposits on the surface thereof;

20 Fig. 5A is a schematic view of a portion of the deposited material after coating and removal of the sphere mask in which there is exposed an array of deposited triangles;

Fig. 5B is a schematic view of the portion of the deposited material after thermal annealing at 800 degrees C in which the particles become more spherical;

5 Fig. 6A is a schematic representation of the pattern generated by two monolayers offset by 30 degrees;

Fig. 6B is a schematic view of a microscopy image of the array of Fig. 6A fabricated with the disclosed method;

10 Fig. 7A is a schematic representation of the pattern generated by two monolayers offset by 10 degrees;

15 Fig. 7B is a schematic representation of a microscopy image of the array of Fig. 7A fabricated with the disclosed method;

Fig. 8A is a schematic representation of an array of spheres on a surface;

20 Fig. 8B represents a coating on top of the spheres of Fig. 8A, which leaves deposits in the interstices between spheres; and

Fig. 8C is a schematic illustration of a freestanding mask with holes therein and the substrate

with corresponding deposits produced after dissolution of the spheres shown in Figs. 8A and 8B.

Detailed Description Of The Preferred Embodiments

5           This invention remedies various deficiencies in the prior art through the creation of an array with long range order by floating particles on a liquid surface. On the liquid surface, the particles may easily rearrange, and their organization into a  
10           monolayer can be promoted with a surfactant. This highly ordered monolayer can then be deposited on a substrate, either by draining the liquid from the container, such that the monolayer deposits on the container floor, or by lifting a substrate up from  
15           below the liquid surface, effectively scooping up the organized array from the liquid. Using these techniques, defect free arrays larger than one square centimeter have been prepared.

20           In addition, another deficiency in the prior art has been to control the orientation of the monolayer with respect to the substrate. It has also been impossible to control the orientation of successive

layers atop the first monolayer. In a preferred embodiment of the present invention, a laser is provided to create diffraction effects that determine the orientation of a floating monolayer. Further, the process can be repeated with a second monolayer and, therefore, the orientation of one monolayer can be controlled with respect to a second monolayer. In this way, ordered multilayer structures can be produced.

It is known in the prior art to use the interstices between particles as a mask to deposit materials onto a substrate. Improvements in the long range order of the particle mask yield dramatic improvements in the utility of the well ordered periodic arrays produced using deposition or etching techniques. For example, long range order provides for optical effects to emerge that are not observed when the periodicity is poor. The strength of the masks formed by the present invention permits the masks to be lifted off the surface.

Additionally, metals such as nickel, iron and cobalt may be deposited in the interstices between particles. These metals are known to be catalytic to

the growth of aligned carbon nanotubes, following the chemical vapor deposition (CVD) techniques of Ren et al. (Science, Vol. 282, pp. 1105, 1998). The combination of this improved masking technique and the CVD method allows production of periodic carbon nanotube structures. Such structures made from carbon nanotubes have important applications, including field emission (particularly for displays), transistors, antennae, sensors and actuators, ion storage materials, chromatographic separation materials, catalyst support materials, photonic materials for optical circuitry, nanoscale grasping devices, and other related applications.

In a preferred embodiment of the invention, and referring now to Fig. 1, there is shown an apparatus for the ordering of a plurality of particles fitted within a container 10. Container 10 provides a draft free, clean environment for deposition onto a substrate 15 in accordance with the present invention. Container 10 is partially filled with a supporting liquid 20.

A pipette 25 is configured within container 10 to deliver a droplet 30 containing the plurality of

particles onto substrate 15. Droplet 30 comprises a suspension comprising a suspension fluid having a plurality of spherical, similarly sized particles suspended therein. In a preferred embodiment of the present invention, the particles are each less than 10 microns in diameter. Droplet 30 is also sometimes referred to herein as a suspension of nanospheres.

Vents 35 within the sidewall of container 10 are opened or closed so as to control the vapor pressure within container 10, and thereby control the evaporation rate of nanosphere suspension 30 delivered within the container.

A second pipette 40 is configured within container 10 to deliver a surfactant 45 to a top surface 50 of the nanosphere suspension 30 contained in container 10.

Referring now to Fig. 1B, there is shown a third pipette 52 configured to adjust the level of supporting liquid 20 within container 10. Third pipette 52 adds a quantity of fluid 20 to the container 10 so as to float the droplet 30 off a top surface 55 of substrate 15. The particles in nanosphere suspension 30 have a density which is lower than, or very close to,



supporting liquid 20 such that nanosphere suspension 30 floats on supporting liquid 20. Additionally, in a preferred embodiment of the invention, the surface of the particles may be treated to be hydrophobic and, therefore, are not wet by the water. The floating particles form a monolayer but do not spontaneously orient with long-range order.

Referring now to Fig. 1C, in a preferred embodiment of the invention, a small quantity of surfactant 45 is added to consolidate the monolayer, which creates long-range order. Surfactant 45 acts to reduce the surface tension of the fluid of the nanosphere suspension 30, and increase adhesion between the particles therein, which in turn promotes the formation of a large, highly ordered monolayer.

Referring next to Fig. 1D, third pipette 52 is used to remove a quantity of supporting liquid 20 from container 10, thereby separating the ordered nanosphere suspension 30 from a surface 60 of supporting liquid 20 so as to leave the nanosphere suspension 30 deposited on the substrate 15, where it can dry. Vents 35 are

adjusted to control the vapor pressure within container  
10 and thereby control drying.

Thus, with the construction disclosed in Figs.  
1A-1D, a suspension of nanospheres 30 is deposited onto  
5 the top surface of a substrate 15, the suspension of  
nanospheres 30 is floated off the substrate, a  
surfactant 45 is introduced to promote the formation of  
a large, highly ordered monolayer, then the ordered  
nanosphere suspension 30 is deposited onto the top  
10 surface of the substrate, and then the suspension fluid  
is dried so as to deposit the ordered monolayer on the  
top surface of the substrate.

In an alternative embodiment of the present  
invention, a substrate 15 lies on a movable platform 61  
15 below the surface of a supporting liquid 20 with  
higher density and substantially immiscible with the  
fluid of nanosphere suspension 30. The nanosphere  
suspension 30 floats on the high density supporting  
liquid 20. As the substrate is slowly raised up from  
20 the supporting liquid 20 into the suspension 30, and  
then into air, the solvent between the spheres  
evaporates, causing forces that act to arrange the

spheres in an ordered fashion. By raising the substrate 15 up through the interfacial layer between the first liquid and the second, only a small amount of the nanosphere suspension 30 is required, as opposed to a sufficient volume to immerse the entire substrate.

In another preferred embodiment of the present invention, the frame 61 holding the substrate 15 is connected between two parallel electrodes, which provide a means for applying an electric field to the substrate. The application of an electric field to a droplet 30 on a substrate 15 alters the wetting angle of the droplet 30, and thereby controls the wetting of the substrate.

In another preferred embodiment of the present invention, the frame 61 holding the substrate 15 is a heating/cooling device so as to control the substrate temperature.

In another preferred embodiment of the present invention, the substrate frame 61 is a piezoelectric element, which can be electrically driven to apply a vibratory force to the substrate 15 so as to promote

the oscillation of the particles and cause them to form into large, well ordered arrays.

In another preferred embodiment of the present invention, an inspection tool 62 is provided above the substrate 15 to determine the state of the array. In the case of larger particles, e.g., above 1 micron, an optical microscope is sufficient to inspect the state of the array formation. For smaller particles, optical techniques may be replaced with other inspection techniques well known to those skilled in the art.

In a further preferred embodiment of the present invention, the array formed by the spheres within the nanosphere suspension 30 are used as a mask to deposit materials on the substrate 15 through the interstitial spaces between adjacent spheres.

In a further preferred embodiment of the present invention, thermal annealing or chemical etching is used to change the morphology of the deposited material.

In a further preferred embodiment of the present invention, a metal, catalytic to the growth of carbon

nanotubes, is deposited through the spheres of the mask.

### EXAMPLES

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#### Example 1

10 A silicon substrate was boiled in distilled, deionized water for 20 minutes to produce a hydrophillic surface. Next, the substrate was placed in a heated sample holder to allow thermal control over the substrate. A volume of fluid containing sufficient spheres to cover a 1 cm<sup>2</sup> area was drawn into a pipette. The polystyrene spheres in this example were supplied from Interfacial Dynamics Corporation, and were 500 nm  
15 in diameter, with sulphatized surfaces. They were shipped in an aqueous solution of 8.2 wt %. The suspension 30 in the pipette was deposited as a droplet on the hydrophilic silicon substrate. The droplet was then covered with a hydrophobic glass cover slide,  
20 causing the droplet to spread over a 1 cm<sup>2</sup> area of the substrate, thereby forming a monolayer. The glass slide served to limit evaporation of the suspension

fluid. Evaporation progressed inwardly from the edge of the droplet, organizing the spheres into a highly ordered monolayer. By limiting the evaporation to occur on one edge only, the evaporation progressed as a front, organizing the monolayer as it went. After the suspension fluid had evaporated, the hydrophobic glass slide was lifted off the surface, revealing the ordered monolayer below.

#### Example 2

Monolayers were prepared using monodisperse polystyrene (PS) particles with diameters of 1040, 925, 496, 217 and 127 nm. All particles were purchased from Microparticles GmbH (Germany) as a 10 wt. % suspension. The PS particles have a density of  $1.05 \text{ g/cm}^3$ , a refractive index of 1.59, and a hydrophobic surface. The standard suspension 30 was diluted with an equal amount of ethanol. The suspension 30 was then ultrasonically agitated for 20-30 seconds in a bath to improve mixing. The spheres have a polydispersity index of less than 0.05.

Oriented (111) p-silicon wafers, boron doped, with resistivity of 1-20  $\Omega\text{cm}$  and thickness of  $525 \pm 25 \mu\text{m}$ , were obtained from SilChem. The surface roughness parameter RA was about 2 nm. These wafers were cut  
5 into 10x10 mm or 5x5 mm squares. Each square was thoroughly cleaned with acetone, and additionally in ethanol, in ultrasonic bath for 1 minute. The substrates were dried in a nitrogen atmosphere.

A solution of PS-latex particles was prepared  
10 using distilled and deionized water from Mili-Q systems. About 4-6  $\mu\text{l}$  of the prepared solution was applied onto the surface of the clean silicon square (which was kept in 10% dodecylsodiumsulfate solution for 24 hours previously) using an Eppendorf pipette  
15 tip. The substrate was then slowly immersed in deionized water, causing the PS particles to float, forming an unordered monolayer on the top surface of the water. To consolidate the monolayer and increase the level of orientation, one droplet of 2%  
20 dodecylsodiumsulfate solution was added. This caused the particles to stick together, forming a large monolayer with a high degree of order. The substrate

was then slowly pulled from water, taking the floating monolayer with it. The monolayer was allowed to dry, in a clean environment. The resulting monolayer is shown in Fig. 2.

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### Example 3

Looking next at Fig. 3, the samples 100 and 105, produced in Examples 1 and 2 above, were placed in an electron beam evaporator 110, and evacuated to  $5 \times 10^{-6}$  mbar. Using a 10kV acceleration voltage, the electrons 112 produced by a tungsten filament 115 were directed into a crucible 118 holding nickel particles 120. Under these conditions, the nickel 120 is vaporized, and deposits upon surfaces in the chamber, including the samples 100 and 105. The evaporation rate was measured and found to be 1nm/s under these conditions. With the PS coating, most of the nickel 120 does not reach the substrate surface 100 and 105. However, and looking now at Fig. 4, in the interstices 125 between particles 130, the nickel 120 sees the substrate 105, and is deposited thereon. The deposits form a hexagonal array of triangular shapes 140 between

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spheres 130. After dissolving spheres 130 in THF (tetrahydrofuran), the remaining pattern 140 on substrate 145 is revealed, as shown in Fig 5A. After thermal annealing, the triangular shaped particles 140 become rounded spherical structures 150, as shown in Fig. 5B.

#### Example 4

A floating monolayer, as created in Example 2, was illuminated with laser light, creating a diffraction pattern on the substrate below. The observed pattern indicates the orientation of the monolayer. The monolayer was deposited on the substrate and dried.

After establishing a new floating monolayer, the orientation was checked again, and adjusted to specific rotation with respect to the first layer. Figs. 6A, 6B, 7A and 7B show resulting multilayers 155, 160, 165, and 170, which have a complex pattern. The angle between each of the layers in Figs. 6A and 6B is 30 degrees. The angle between each of the layers in Figs. 7A and 7B is 10 degrees.

Example 5 Referring now to Figs. 8A-8C, there is shown a sample 175 prepared in a manner similar to Example 2, coated with metal 180 as described hereinabove (Figs. 8A and 8B). The amount of metal deposited was  
5 sufficient to create a film thickness equivalent to half of the diameter of spheres 185. After deposition, spheres 185 were dissolved in THF (see Fig. 8C). The metal that had been deposited atop spheres 185 separates from substrate 190 upon dissolution of  
10 spheres 185 and creates a freestanding metal film, which has holes therethrough. This process creates a mask 195 that can be used by other processes.